Gas Chromatographic Separation of Oxygen-Containing Terpene Compounds on Low Temperature Columns

SIR: James and Martin (*2*) have shown the fundamental relationship between retention volume and the amount of liquid phase present in a gas chromatographic column. Ring (*5*) has demonstrated on a conventional Celite column that retention times decrease without loss of resolution, and fraction peaks become sharper with a decreasing amount of liquid phase. Hishta, Messerly, and Reschke (*1*) employed columns of 60- to 80-mesh glass beads with less than 0.3% liquid phase to separate high boiling ketones and hydrocarbons. They obtained good resolution and short retention times at temperatures as much as 150° C. below the boiling points of the samples. Littlewood (*3*) and Pollard and Hardy (*4*) obtained good results with similar columns. In the present study columns packed with glass beads containing low concentrations of stationary phases were explored for the separation of various oxygen-containing terpenes which are frequently found in spice oils. Low temperatures and retention times and inert solid supports are desirable because of the tendency of terpenes to decompose or isomerize at elevated temperatures, particularly when in contact with foreign substances such as acids or alkalies.

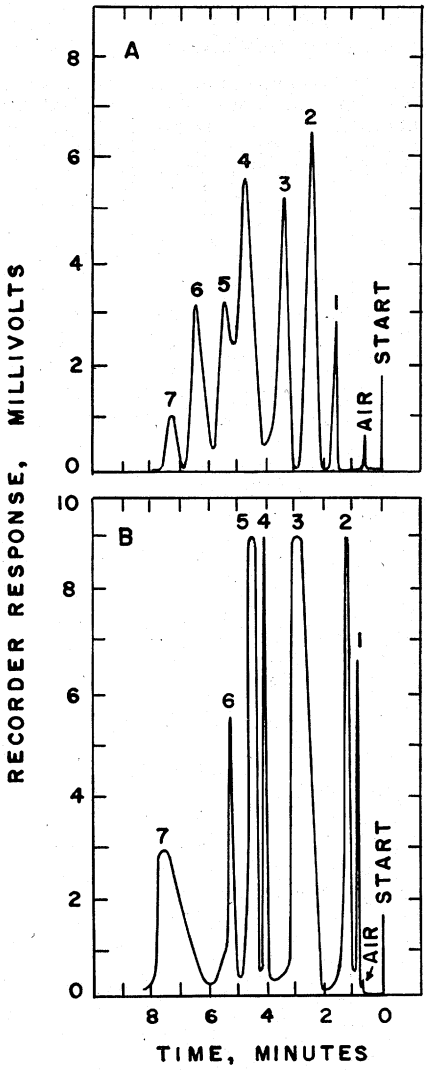

Figure 1. Gas chromatograms of terpene alcohols

2. Linaloöl, 198° C.; 3. Menthol, 216° C.; 4. α-Terpineol, 218° C.; 5. Citronellol 222° C.; 6. Nerol, 225° C.; 7. Geraniol, 229° C. (Peak 1 was the ether, Cineole, 177° C.)
A. 0.20% Dow Corning 710 on glass beads at 90° C.
B. 0.125% Hyprose S.P. 80 on glass beads at 90° C.

EXPERIMENTAL

Equipment. A Research Specialty Company Model 601-1 oven served as the heating unit, and a Gow-Mac two-filament thermal conductivity cell served as the detector with a constant voltage regulator to control the heating of filaments. The recorder was a 10-mv. Leeds and Northrup, type G, instrument with 1-second response and a chart speed of 0.5 inches per minute. Emerging components were collected with a Model CH6-H fraction collector equipped with type D cells of 0.1-mm. thickness and manufactured by Connecticut Instrument Co. A Perkin Elmer Model 21 infrared spectrophotometer was used for sample identification.

Preparation of Columns. Stainless steel tubes, 6 feet in length and 1/4-inch o.d., containing either a polar or a nonpolar stationary phase on 60- to 80-mesh glass beads were used. The concentration of the polar stationary phase, Hyprose S.P. 80, was 0.125% and the nonpolar phase, Dow Corning 710, was 0.2%.

Procedure. Three terpene mixtures were chromatographed on a Dow Corning 710 and on a Hyprose S.P. 80 column, under the conditions listed in Table I. The terpene mixtures were six alcohols, eight aldehydes, and three esters.

Emerging components were trapped in a cooled fraction collector which deposits the compounds directly in an ultramicro type D infrared absorption cell. After the fraction had been collected, the inner cell of 0.1-mm. thickness was filled with carbon tetra-

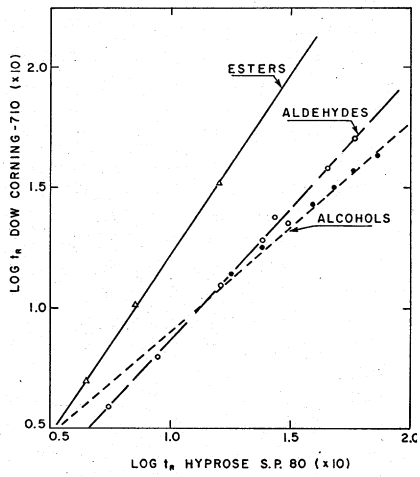

Figure 2. Determination of nature of oxygen-containing terpenes by comparing their behavior on two different columns

Table I. Composition of Mixtures and Relative Retention Times of Components

The experimental conditions were: oven temperature, 90° ± 1° C.; detector temperature, 100° ± 1° C. for the Silicone 710 column and 110° ± 1° C. for the Hyprose S.P. 80 column; injection block temperature, 210° ± 2° C.; carrier gas flow at 5 p.s.i., 70° F., 40 ml. per minute; column length, 6 feet; inert support, glass beads of mesh size 60–80; sample size, 1 μl.

Compound	Relative Retention Times: Dow Corning 710	Relative Retention Times: Hyprose S.P. 80
Alcohol Mixture[a]		
Linaloöl	1.39	1.78
Menthol	1.78	2.39
α-Terpineol	2.72	3.94
Citronellol	3.16	4.78
Nerol	3.78	5 78
Geraniol	4.28	7.26
Aldehydes Mixture		
Benzaldehyde	0.39	0.56
Caproic aldehyde	0.62	0.89
Methyl heptanone	1.23	1.61
Caprylic aldehyde	1.91	2.44
Citronellol	2.24	3.11
Capric aldehyde	2.41	2.67
Citral	3.81	4.50
Cinnammic aldehyde	5.02	5.83
Esters Mixture		
Linolyl acetate	0.50	0.44
Geranyl acetate	1.05	0.72
Neryl acetate	3.28	1.61
Reference Standard (Tetraline)	1.00	1.00

[a] Each mixture contained approximately equal amounts of each component.

chloride, and the solute was identified by comparison of the infrared spectrum with spectra of authentic reference materials.

RESULTS AND DISCUSSION

The observed relative retention times of the three types of materials are listed in Table I. All terpenes were eluted from both columns in less than 8 minutes. The retention time of tetralin (taken as 1) was the reference standard. Under the experimental conditions described, the specific retention volume per gram of liquid phase was 264 ml. per gram for Dow Corning 710 and 164 ml. per gram for Hyprose S.P. 80. As shown in Figure 1, the complete separation of alcohols was achieved with Hyprose S.P. 80 but not with Dow Corning 710 column. The aldehydes and esters examined, however, were completely separated in either column.

Peak 7 in Figure 1B (geraniol) is skewed toward peak 6 (nerol, the *cis* isomer of geraniol). The infrared curve for peak 7 is qualitatively very similar to that for pure geraniol. Both isomers exhibit medium strength absorption bands at 1670 cm.$^{-1}$ but only the *trans* form, geraniol, has a band at about 890 cm.$^{-1}$ The ratio of A_{890} cm.$^{-1}$ to A_{1670} cm.$^{-1}$ for pure geraniol was approximately 0.8 whereas this ratio for fraction 7 was lower, indicating the presence of some nerol in fraction 7.

In general, the behavior of three types of compounds was quite different on the two columns. For example, with the exception of the esters shown in Table I, all compounds had longer retention times on the Hyprose column. With the Dow Corning 710 column, all the terpenes within one mixture were eluted in the order of their boiling points, but with the Hyprose S.P. 80 column this was not the case.

In Figure 2 the logarithms of the relative retention times observed on the two columns are plotted against each other. The resulting points for the esters, aldehydes, and alcohols lie approximately in three different straight lines. Determination of the chemical nature of oxygen-containing terpenes can be facilitated in many cases by comparing their behavior on a polar and a nonpolar column.

LITERATURE CITED

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Work was supported in part by funds from the American Spice Trade Association. Mention of a specific product does not constitute endorsement of that product over similar ones not mentioned.